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Closed Cycle Textile Dyeing Extended Evaluation of Full-Scale Hyperfiltration Demonstration

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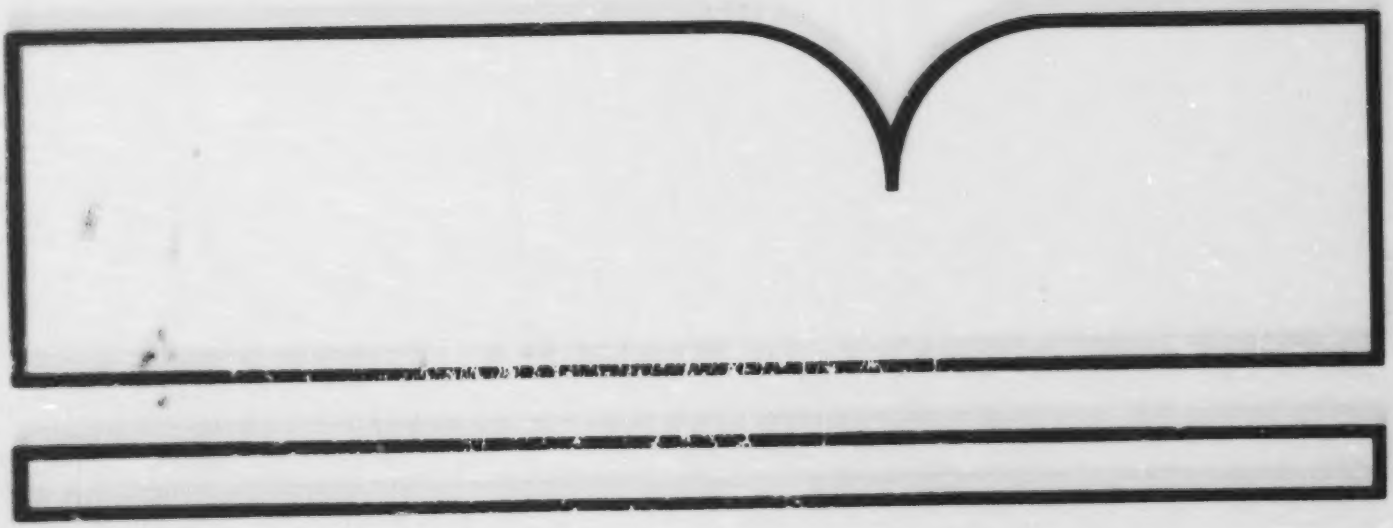

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CLOSED CYCLE TEXTILE DYEING: EXTENDED EVALUATION OF FULL-SCALE HYPERFILTRATION DEMONSTRATION

by

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16. ABSTRACT The report describes the hyperfiltration (HF) system, gives data from several chemical recycle tests, and discusses HF as a dye recovery technique. The configuration of the HF system is set aside for possible future use when economic and regulatory requirements change. In this off-line configuration, privately funded studies of reuse and membrane performance are continuing. HF is a membrane separation technique that has been used successfully to desalinate natural water. Because energy, process chemicals, and water are discharged from industrial processes in large quantities, recycle has been studied in a series of government sponsored research projects. Research results led to the current project of joining a full-scale HF system (with operating dye range) to an integrated production unit. The dye range is a multipurpose unit with a variety of effluents from the preparation and dyeing of a variety of textile fabrics. High temperature membranes of hydrous zirconium oxide and polyacrylic acid dynamically formed on porous, sintered, stainless-steel tubular supports were installed as a demonstration unit. Over 2 million m of fabric was produced with recycled water. Two 4000-m lots of fabric were produced with the recycled chemical concentrate. The demonstration project was extended to further study and develop the recycle of the chemical concentrate.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Zirconium Oxides	Pollution Control	13B	07B
Textile Industry	Polyacrylic Acids	Stationary Sources	11E	11I
Dyeing		Hyperfiltration	13H	
Circulation		Membrane Separation	14G	
Fluid Filters			13K	
Membranes			11G, 06C	

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ABSTRACT

Hyperfiltration (HF) is a membrane separation technique that has been used successfully in desalination of natural water. Because energy, process chemicals and water are discharged from industrial processes in large quantities, recycle has been studied in a series of government sponsored research projects. The results of the research led to the current project of joining a full scale HF system with operating dye range into an integrated production unit. The dye range is a multi-purpose unit having a variety of effluents from the preparation and the dyeing of a variety of textile fabrics.

High temperature membranes of hydrous zirconium oxide and polyacrylic acid dynamically formed on porous sintered stainless steel tubular supports were installed as a demonstration unit. Over two million meters of fabric were produced with recycled water. Two 4000 meter lots of fabric were produced with the recycled chemical concentrate. The demonstration project was extended to further study and develop the recycle of the chemical concentrate.

The results of the demonstration project indicated a positive rate of return with savings from recycle more than offsetting capital and operating costs. The actual payout time depends primarily upon the value of the chemicals and the practicality of their recycle.

This report describes the HF system, presents data from several chemical recycle tests and discusses hyperfiltration as a dye recovery technique. The configuration of the hyperfiltration system as set aside for possible future use when economic and regulatory requirements change. In this off-line configuration, privately funded studies of reuse and membrane performance are continuing.

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ENGLISH-METRIC CONVERSION TABLE*

To Convert From	To	Multiply by
Inch	Meter	2.54×10^{-2}
Feet	Meter	3.05×10^{-2}
Square inch	Square meter	6.45×10^{-4}
Square feet	Square meter	9.29×10^{-2}
Cubic feet	Cubic meter	2.83×10^{-2}
Gallon	Cubic meter	3.79×10^{-3}
Pound	Kilogram	4.54×10^{-3}
Pound per sq. inch (psi)	Atmosphere	6.80×10^{-2}
Horsepower (Hp)	Watt	7.46×10^{2}
Gallon per day	Cubic meter per day	3.79×10^{-3}
Gallon per minute (GPM)	Cubic meter per day	5.45
Gallon per sq. ft.-day (GFD)	Cubic meter per sq. meter-day	4.10×10^{-2}
Gallon per minute per sq. ft.	Cubic meter per sq. meter-day	5.87×10^{1}

*The units most familiar to the projected readership of this report have been maintained.

ACKNOWLEDGEMENTS

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This demonstration is an interagency program and thus benefited from the guidance of Robert Hendriks, U. S. Environmental Protection Agency, as Principal Project Officer; John Rossmeissl and William Sonnett, Department of Energy, and Frank Coley, Department of the Interior, as Project Officers; and Robert Mournighan, U. S. Environmental Protection Agency, as Technical Advisor. J. S. Johnson, Jr. has served as membrane technology consultant on this and all the previous related research and development projects.

CARRE, Inc. provided overall program management. The contributions of staff members of CARRE, Inc. are acknowledged. Staff members making major contributions are J. L. Gaddis, and H. G. Spencer; Donald K. Todd and Daniel A. Jernigan, engineers; and Don King and Cindy Cochran, technicians.

GLOSSARY

CONCENTRATE - the fluid that does not permeate the membrane and thus contains the solute species that do not pass through the membrane.

CONTINUOUS DYE RANGE - the equipment components arranged sequentially such that fabric is dyed as it moves continuously through the range components. Other preparation and finishing operations can be performed on the dye range such as bleaching and scouring.

DRUG ROOM - the room where the dye formulations are mixed in 100 liter to 4,000 liter batches for transfer to the dye pad during the dyeing production.

DYE FORMULATION - a solution of dyes and chemicals applied to fabric as it moves through the continuous dye range. The chemicals include a thickener (guar gum), surfactants, and in some cases, dye solvents.

DYE PAD - the 50 liter tank in which the dye formulation is applied - "padded" to the fabric.

FLUX - the volume of permeate generated per unit of membrane area per unit of time.

HYPERFILTRATION - a membrane separation process operating on the principle of selective diffusion through a semi-permeable membrane achieved by pressure differential.

HYPERFILTRATION (HF) UNIT - a component of the recovery system consisting of ZOPA membranes arranged in a Single Pass configuration.

MEMBRANE FOULING - a decrease in flux that is not an instantaneously reversible effect of controlled operating variables. Fouling is usually categorized as (1) an alteration in the membrane due to a chemical reaction with the waste stream components or (2) an accumulation of a deposited material.

MODULE - a group of membrane segments contained in a housing suitable for collecting permeate. Membrane segment connections are external to the housing.

PERMEABILITY - the volume of permeate generated per unit of membrane area, time and pressure across the membrane. (Flux per unit of pressure across the membrane.)

PERMEATE - the fluid that passes through the membrane and thus contains the dissolved materials that pass through the membrane.

RECOVERY - the fraction of fluid exposed to the membranes that becomes permeate.

RECOVERY SYSTEM - the equipment that collects waste fluid from the dye range, processes this fluid with a membrane unit, and makes available hot clean permeate for use as washwater on the range and concentrate for use in dye formulations or for disposal. This system includes tanks for the wastewater, recycle water and concentrate; pumps; hyperfiltration unit and controls.

REGENERATIVE HEAT EXCHANGERS - a unit used to exchange thermal energy between incoming wastewater and outgoing permeate. Net effect is to operate the membrane unit at a higher temperature than the dye range washers when operated with a small steam heater applied to the wastewater after this heat exchanger.

REJECTION - the fraction of a particular material specie that does not pass through the membrane.

SEGMENT - the porous tube lengths connected serpentinely with small radius u-bends. The two ends of the segment protrude through one end of a module for connecting with other segments in the desired system configuration.

SINGLE PASS - a patented (U.S. Patent No. 4200533 of CARRE, Inc.) membrane arrangement such that entering fluid is separated into permeate and concentrate streams without the concentrated fluid ever being routed upstream of a segment of membrane area through which it has passed.

STRIKE - the dyeing of a small piece of fabric to determine shade and other properties prior to production.

ZOPA MEMBRANE - a high temperature dynamic membrane formed of zirconium oxide/polyacrylic acid membrane (U.S. Patent Nos. 3,431,201; 3,449,245; and 3,503,789).

SECTION 1

INTRODUCTION

The technical feasibility of using hyperfiltration (HF) to renovate textile wastewater for direct recycle was shown in a series of research projects conducted as part of a cooperative program between the textile industry and the U. S. Environmental Protection Agency beginning in 1972.

The current project demonstrates, at full scale, the use of hyperfiltration with a production dye range. This project is funded by a cooperative agreement between the Environmental Protection Agency, the Department of Energy, the Department of the Interior and La France Industries, a Division of Riegel Textile Corporation.

The wide scale implementation of hyperfiltration to recycle hot process effluents would have a large impact on pollution abatement. The cost of achieving this pollution abatement with hyperfiltration will be offset by the combination of savings from the simultaneous recovery of energy, water, and chemicals. If subsequent waste treatment is required, instead of reuse, for all or a portion of the chemical residue, the cost of this treatment will probably be less because of the volume reduction achieved by hyperfiltration.

The renovation and recycle of hot process water has been demonstrated (1). This report summarizes information about chemical reuse obtained during a 12 month extension of the original project period. Some of the background material included in the final report (1) on the initial phases of the project is included here for the convenience of the reader.

HYPERFILTRATION

Hyperfiltration is a membrane separation process operating on the principle of selective diffusion through a semi-permeable membrane, achieved by pressure differential. Since the separation is achieved without a change of phase, membranes are inherently energy efficient. The optimized Single Pass arrangement (U. S. Patent No. 4200533 of CARRE, Inc.) which requires no recirculation of any concentrated material, utilizes approximately four BTU's per pound of water passing through the membrane. The energy used is generally electrical energy to operate the pumping system. Converted to the equivalent thermal basis of 10,500 BTU/kilowatt hour, this would be approximately 12 BTU's per pound of permeate produced. Change of phase technologies, such

as freezing and evaporation, require four to forty times as much energy per pound of water separated.

Initial interest in membrane separation was largely directed to desalination of sea and brackish water. Attempts to utilize the technology in industrial situations encountered limitations dictated by temperature and composition of the typical individual waste streams. The innovation of zirconium oxide/polyacrylic acid (ZOPA) membranes (U. S. Department of Energy Patent No's: 3,431,201, 3,449,245, and 3,503,789) dynamically formed on sintered stainless steel tubes (NASA Patent Pending), relaxed many of the limitations. Dynamically formed membranes can operate under a wide range of corrosive conditions at high pressures and temperatures, are able to withstand high suspended and dissolved solids and are not subject to bacteriological attack. These high temperature membranes are utilized in the current hyperfiltration demonstration system.

PREVIOUS STUDIES

Three previous studies led to this full-scale demonstration. The first study (2) begun in 1972 involved the pilot-scale separation of composite wastewater from a beck dyeing process and a full-scale reuse of hyperfiltration permeate and concentrate at this site. Polyamide (hollow-fine fibers), cellulose acetate (spiral and tubular), and hydrous Zr(IV) oxide-polyacrylate membranes were used. Eighteen production dyeings involving a total of 1348 m of cloth were carried out in a production dye beck.

The purified permeate water was a satisfactory substitute for normal process water in all production dyeings for water recoveries ranging from 75 to 90%. Membranes used in the renovation of the wastewater had conductivity rejections of 65 to 95% and color rejections from 86 to > 99%.

It was also technically feasible to reuse all the concentrate. In 11 production dyeings over a 700 m of cotton velour fabric was produced, graded as first quality, and sold commercially. In 10 tests standard shades were produced with an average dyestuff savings of 16%.

The second study (3) involved composite wastewaters obtained from the several processes occurring in a dyeing and finishing plants were separated by hyperfiltration, and the cumulative permeate and concentrate of a 90% recovery run was tested for reuse as process water in laboratory dyeing. Precast and dynamically formed membranes were used at eight dyeing and finishing plants. The processes encountered were: dyeing of nylon using pre-metalized dyes, dyeing of acrylic fabric using basic dyes, and the scouring, desizing, and dyeing of cotton and polyester. In all cases the product water was acceptable for replacement of process water as determined in laboratory dyeings using standard production evaluations. Analyses indicated higher COD and dissolved solids and lower concentrations of metals in the permeate water than in the fresh plant-process water. The concentrate from the premetallized dye process was suitable for dyeing very deep shades upon addition of appropriate dyes.

Laboratory dyeing tests using concentrates from the other processes were unsuccessful. Perhaps this result is not surprising because the concentrates were obtained from a feed containing a composite of effluents from the plant processes and not from a single process.

The first two studies dealt with renovation of the composite wastewater from the dyeing and finishing plants. Because of the obvious advantages for chemical reclamation and energy conservation, a third study (4) evaluated hyperfiltration for direct recycle of unit process effluents. Five major water and energy consuming preparation and dyeing processes were studied with high temperature hyperfiltration membranes. The permeate produced by the membranes was again found to be universally usable as process water. In some cases the reuse of the concentrate from the individual process effluent streams was estimated to be practical.

ENERGY RELATED PROBLEMS

About 2 trillion gallons of hot water are discharged by industry each year. Literally about 6% of all the energy consumed by industry goes down the drain. Much of this hot water is "contaminated" with chemicals and other dissolved or suspended material which not only constitute a hazard to the environment, but represent an additional "waste" of materials which requires substantial energy to produce or replace. Additionally, much energy is expended by industry to remove water from the industrial waste stream to achieve desired levels of chemical concentration to permit reuse, or to reduce the volume of materials to be stored, processed, or transported.

Many, if not most, industrial situations in which the manufacturing process involves industrial waste water have similar characteristics:

1. A contaminate level that requires reduction to permit hot water recycle; and/or

2. A content of dissolved chemicals or suspended solids that requires concentration to facilitate the recovery or reuse of the chemicals.

Often, the simple separation of the water and solids in the typical industrial waste stream will permit the simultaneous recycle or recovery of both the water and the solids.

Despite these common characteristics, each industrial waste stream contains unique features which must be considered not only as to the type of separation but the economic soundness of a program of recycle and recovery. The uniqueness may be in the type of corrosiveness (i.e., acid, base, oxidant, etc.); the specific separation required; the type of foulants which may lead to reduction of the performance of the separation equipment; and other characteristics of the particular industrial waste stream. The ultimate impact of using HF in industry could approach 5% savings of present energy consumption just in the single area of hot water recycling.

Additional energy savings could probably be effected by reducing the required amount of evaporation, as well as by recovering of the chemicals presently being literally thrown away. Additional energy savings will result from reduced pollution and the reduced energy consumed in pollution treatment. The estimated potential in energy and material resource conservation by recycle in the U. S. textile industry based on a 1978 study (3) is shown in Table 1. This energy conservation for the textile industry is equivalent to approximately fifteen million barrels of oil per year. The total value of energy and material conservation is estimated to be nearly one billion dollars per year. The 1984 price of dyes and other chemicals varies widely from those of 1978 and in some cases may be as much as 10 times the $2.3/kg shown in Table 1 (5).

TABLE 1. POTENTIAL ENERGY AND MATERIAL RECOVERY FOR THE U. S. TEXTILE INDUSTRY

	Water Discharge (10^3 m^3/d)	Dyes (10^3 kg/d)	Auxiliary Chemicals (10^3 kg/d)	Salt (10^3 kg/d)	Process Thermal Energy (10^9 BTU/d)
1978 Study Total[a]	120	27	13[b]	12	38
Industry Total	2700[c]	1000	270	264	784
Recycle Potential	2400	60	222	220	352
Estimated Annual Savings[d] ($ x 10^6/yr)	120	158	36	2.6	616

(a) Reference 3
(b) Exclusive of 80,000 kg. of NaOH used daily at these plants.
(c) 1972 census of manufacturers, assuming 250 days/year.
(d) Unit costs: water @ \$0.2 m^3; dye @ \$2.3/kg; auxiliary chemicals @ \$0.66/kg; salt @ \$50/1,000 kg; process steam @ \$7/10^6 BTU.

PURPOSE AND SCOPE

The purpose of this extension period was to gain additional information on reuse of the dyes and chemicals removed from the waste wash water by hyperfiltration. Additionally, the performance of the hyperfiltration unit was monitored to evaluate membrane washing, membrane durability and on site membrane re-coating.

The scope of the study during the extension period included full-scale production of first quality velour fabric dyed utilizing chemicals reclaimed from the waste wash water. Because of the lack of production of non-cellulosic fabric for which a good payout is achieveable and because of the delay in the installation of a color matching computer, the number of full-scale tests was limited to selected cases to demonstrate the concept. Laboratory scale reuse tests and computer generated color matches were included in the study.

METHOD OF STUDY

This project was conducted using the existing hyperfiltration equipment with production lots of fabric selected to represent the value of chemical recycle. The amount of dye in the hyperfiltration concentrate was evaluated by using standard production equipment to dye cloth samples for which shade depth was measured. Manual shade matching was used to develop the formulation to be used in the initial full-scale reuse tests. Later in the project period, automatic color sensing equipment and a computer were used to calculate shade matching formulas.

Regularly scheduled production was accomplished with recycle dyes and chemicals after additions were made to the formulations to achieve color matching. Standard finishing and inspection procedures were followed with the material produced in these reuse tests.

OVERALL RESULTS

A Phase I design report was published (6). The two major results of the study and design activities of Phase I were:

1. The selection of the continuous dye range instead of the dye becks for the full scale demonstration.

2. The determination that hyperfiltration had the potential to achieve a practical approach to zero discharge with a positive rate of return on the required investment.

During Phase II and Phase III, over a million meters of standard width (1.4 meters) velour fabrics were washed with recycle water during routine production. Tests of reuse of dyes and chemicals with production lots totaling 4,000 meters of velour were achieved.

During Phase IV, the extension period covered by this report, the hyperfiltration unit was operated with many of the same membranes initially installed. The membranes in one module were removed and recoated, _in-situ_, to demonstrate this procedure.

Washing procedures for both of the major dye classes in use at La France, basic dyes and direct dyes, were developed. The fouling rate and average flux were not improved from that reported at the end of Phase III, however.

Reuse of dyes and chemicals were shown in laboratory and full-scale production to be technically feasible. Full-scale production reuse tests were conducted producing first quality goods from mixtures of dyes recovered from a series of production lots as well as dyes recovered from a single production lot. The economics for La France are not attractive because of the relatively low cost of direct dyes that comprise the major percentage of production at this facility. A color matching computer was used demonstrating the procedure for developing formulations for color matching.

The capacity of the HF unit is limited by fouling to a time average of about 50% of design capacity. At current levels of chemical reuse and HF capacity there is a small net savings of approximately $16,000 per year. This savings level is not sufficient to warrant full scale operation of the HF unit.

The studies to improve HF performance and chemical reuse are continuing with private funding. The HF unit thus remains available should production change to the more expensive dyes (_e.g._ to acrylic or nylon fabric) or should environmental discharge requirements be strengthened particularly in the area of color removal.

SECTION 2

CONCLUSIONS

For thirty-six months a production size HF unit has been integrated with a manufacturing dye range. Full scale recycle of hot wash water from a dynamically-formed ZOPA membrane hyperfiltration system has been utilized with the production of cotton velour fabric. More than two million meters of fabric have been washed with recycled water with no significant effect on fabric quality.

Reuse of dyes and chemicals were shown in laboratory and full-scale production to be technically feasible. Full-scale production reuse tests were conducted producing first quality goods from mixtures of dyes recovered from a series of production lots as well as dyes recovered from a single production lot. The economics for La France are not attractive because of the relatively low cost of direct dyes that comprise the major percentage of production at this facility. A color matching computer was used demonstrating the procedure for developing formulations for color matching.

For more than forty months, ZOPA membranes have remained stable with respect to rejection. It has been demonstrated that the stainless tubing can be completely stripped and that new membranes can be formed in-situ. Membrane cleaning methods have been developed for both the basic and direct dye formulations in use at La France. However, the production of permeate has been limited to about 50% of the design capacity by membrane fouling.

Disposal, as distinct from reuse, of HF concentrate was studied. The technical feasibility of incineration after further concentration by HF and drying was demonstrated. Thus a method of complete on-site disposal was shown to be technically feasible. At La France, the HF concentrate is treated in the biological treatment system with no apparent problems.

The experimental results and economic projections indicate that the most favorable situation for the application of HF is the one where there are simultaneous and significant benefits for water, energy, and chemical recovery and where significant waste treatment costs can be abated by reuse for volume reduction.

For example, a new plant in a city in a water-short region dyeing nylon velour would find HF very economical. The value of water and the charges for sewage could be 2 to 5 times that at La France. The value of pre-metalized dyes could be 5 to 10 times the direct dyes normally in the wash water at La France.

The value of direct dyes and the cost savings in water and waste treatment at La France are not sufficient to justify continued operation of the HF system on a commercial basis. The HF unit has been placed in a stand-by configuration to be available for possible future use when economic conditions or regulatory requirements change, particularly in the area of color removal. With private funds, the studies of reuse and membrane performance are continuing.

SECTION 3

RECOMMENDATIONS

The results of the demonstration project can be enhanced by further development of techniques for chemical reuse and further development of techniques to improve performance of the hyperfiltration unit.

It is recommended that this full-scale installation be used in the future to:

(1) continue full scale reuse testing of HF concentrates combined with unspent dye liquors;

(2) develop and evaluate new membranes for lower fouling and for better rejection of basic dyes.

It is improbable that reuse of 100% the HF concentrate will ever be practical due in part to scheduling and storage difficulties. Thus it is recommended that this full-scale production unit be used to further study HF concentrate disposal. HF concentrate constitutes a new form of industrial effluent. The disposal of HF concentrate because of the small volume and high concentration may be amenable to disposal by chemical processes not normally considered for waste treatment, such as evaporation and incineration.

The results of this demonstration of high temperature dynamically formed HF membranes on reuseable porous stainless steel tubes are applicable to many industrial situations. Porous sintered metal dynamically coated with select membranes can be widely applied to hot (>100° C), corrosive, and suspended solids-laden industrial effluents. The dynamic formation technique is inherently versatile permitting _in-situ_ membrane replacement and the use of a wide variety of membrane materials that can be selected for specific separation requirements. It is recommended that research in membrane tailoring for selected important industrial categories be undertaken.

SECTION 4

TEXTILE PROCESS DESCRIPTION

The textile processes involved in this project are conducted on a continuous dye range. The range and its operation are described in this section. The chemical characteristics of the wash water effluent, _i.e._, the waste wash water supply to the hyperfiltration unit, are also presented.

DYE RANGE

The continuous dye range is also used for bleaching and scouring. The range consists of a dye applicator, a spiral atmospheric steamer, and a washing section shown in Figure 1. Most of the production is velour upholstery fabric for which there are stringent light fastness and crocking (color abrasion) requirements. The types of fibers processed include cotton, acrylic, nylon, rayon, and polyester as well as their blends. The dye range is fully automated to control cloth speed and wash water temperature and flow rate. The range processes fabric from 9 to 36 meters per minute depending on the fabric type and the process details. The range is operated three shifts per day, five to seven days per week.

Fabric moves sequentially through the equipment components beginning with the dye pad. Dye formulations are mixed in the drug room and pumped to the pad where they are applied to the fabric. The applicator is a 50 liter tank in which the fabric is saturated. Excess dye and auxiliary chemicals are removed from the fabric by squeeze rollers as it leaves the pad and before it enters the steamer. The temperature is maintained at 100\o~C in the steamer. The steamer holds approximately 150 meters of fabric so range speed is set to achieve the time in the steamer for the particular fabric and dye combinations.

Fabric moves from the steamer to a series of washers where excess dyes and auxiliary chemicals are removed. The washing train consists of jet washer, dip box, and two rotojet washers. Squeeze rollers follow the dip box and each rotojet washer. The jet washers and the two rotojet washers incorporate large recirculation flow rates which pass through 100 mesh stainless steel screen filters. The majority of the wash water is supplied to the second rotojet which counterflows to the first rotojet which in turn counterflows into the jet washer. A smaller amount of water enters the dip box and counterflows to the jet washer. The jet washer overflow becomes the

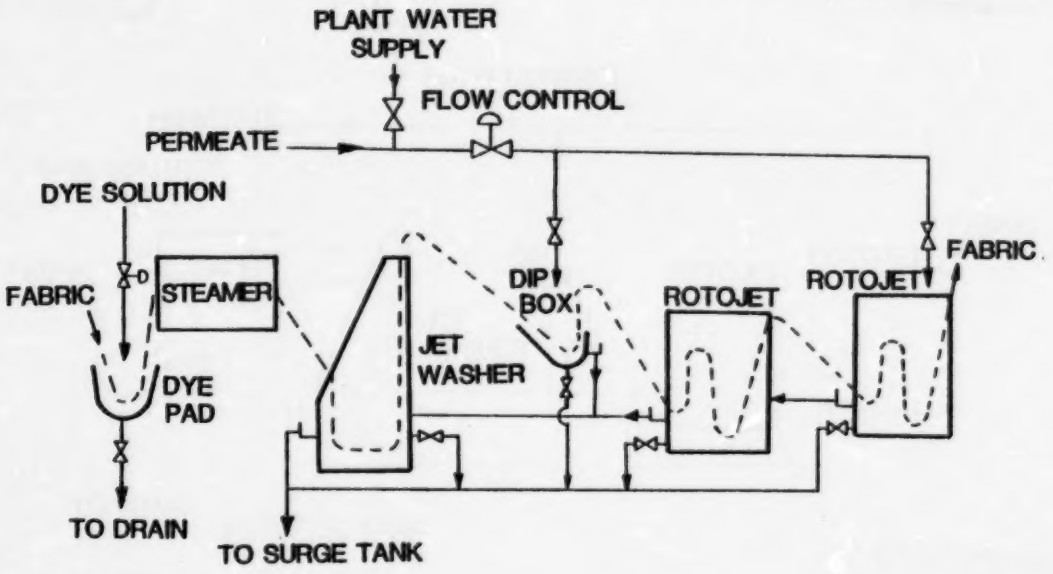


Figure 1. Continuous Dye Range Schematic.

supply to the hyperfiltration system. Water flow to the range is automatically controlled and can be set at the range operator control panel. Steam is injected into the water within the washers to maintain the controlled process temperature in the range of 60 - 85\o~C.

When the range is used for bleaching, the operation is essentially the same as when dyeing. The bleach formulation is mixed in the drug room and pumped to the pad where it is applied to the fabric. The active bleaching agent is reacted in the steamer and essentially only auxiliary chemicals are removed in the washing. The scouring operation does not use the pad. The fabric is simply treated in the steamer and washed.

PRODUCTION CHARACTERISTICS

The characteristics of the production influences the feasibility of water recycle and chemical reuse. The size of the production lots and hence the frequency of color and dye type changes is important in determining (1) the difficulty of scheduling color matching procedures, and (2) the value of dyes in each batch of HF concentrate and residual dye collected. The cost per liter varies by a factor of about 10 to 1 from the lightest shade direct dye to the darkest basic/direct dye formulations. Pre-metalized dyes can be even more valuable. Reactive dyes, however, have essentially no value for reuse since the reactions are not easily reversible.

The monthly average values of normalized lot size and production, based on yardage percent, are presented for 20 months from January 1980 through September 1981 in Figure 2. The data indicate a consistency with 50 to 80 percent of all production involving the use of direct dyes only. The production involving some of the more expensive dyes was steady at about 20 percent for more than a year but dropped in late 1981 to less than 10 percent. The production utilizing basic dyes has not increased through 1983.

A typical production profile for a 24-hour period is presented in Figure 3. The production rate varies depending on fabric weight and other parameters. It is not important to report exact production data (which is confidential) to illustrate the essential facts (1) that production changes are frequent and (2) the majority of production time is with direct dyes. Production time includes the necessary period between different lots. The open time intervals shown in the plot are for machine cleaning or other non-production activity. The production data is summarized for a longer period in 1982 in Table 2. For the period of this data the basic dyes were utilized 25 percent of the time. Later the use of basic dyes decreased. The average number of production lots per shift is over 7; almost once each hour.

The direct dyes are highly rejected by the ZOPA membrane so that the HF unit produces good quality permeate. The direct dyes are technically easy to reuse but the value of the direct dyes is relatively low. The reactive dyes are also easy to reject and hence cause no problem for permeate recycle. The basic dyes are less well rejected, 96 percent instead of 99 percent, resulting in difficulty in permeate recycle about 1 percent of the time\(5)~. The

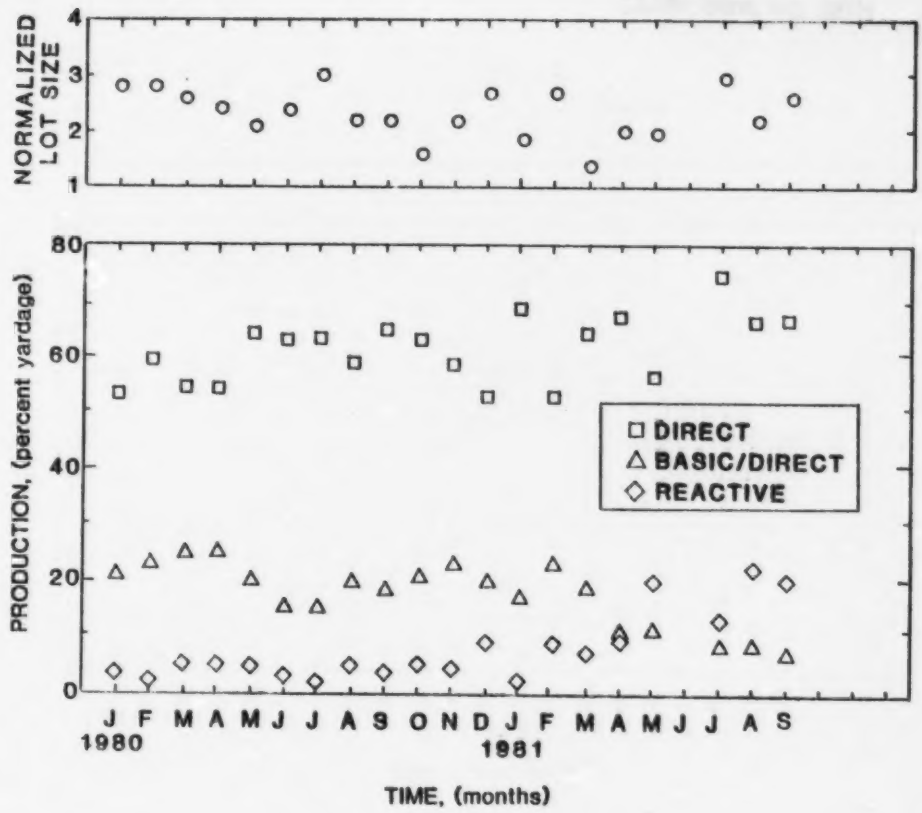


Figure 2. Averaged Monthly Production Characteristics for Lot Size and Dye Class. (Lot size is normalized by a proprietary constant. Percent of total production for the predominant dye classes at La France are shown on a weekly basis.)

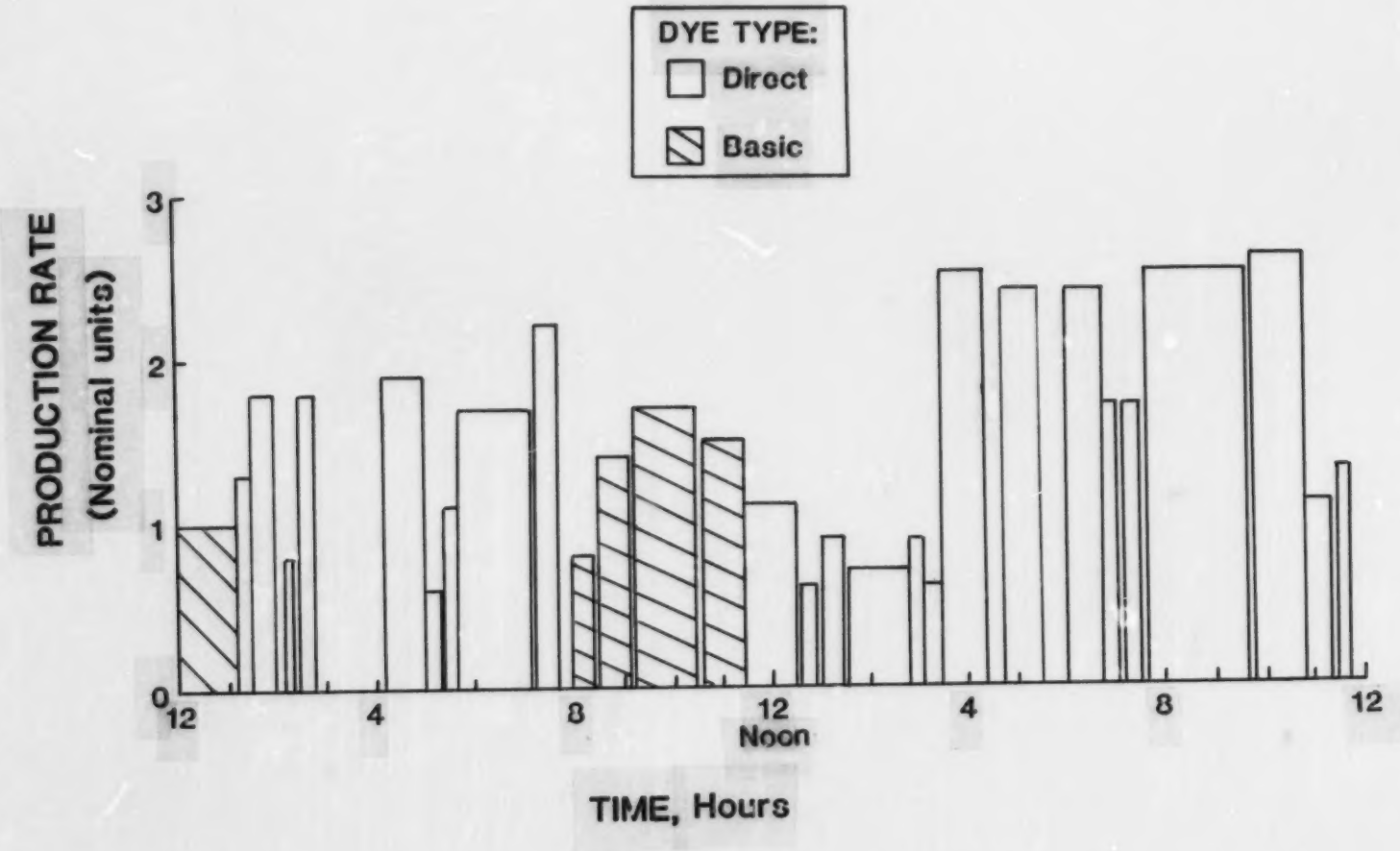


Figure 3. Typical Production Profile for the Dye Range.

Table 2. Typical Production on Dye Range for a Period in 1982

Number of dye lots:	552
Avg. number of lots dyed per shift	7

50% of the lots were less than 40 minutes.
50% of the fabric was in lots of greater than 2 hours.

Percentage of Dyeing Production Time by Dye Type	
1. Direct	58
2. Acid	1
3. Basic	39
4. Disperse	1
5. Reactive	1

Percentage of Dyeing Production Time Based on Yardage	
1. Direct	68
2. Automotive	1
3. Basic	25
4. Disperse	1
5. Reactive	5

value of the basic dye formulation can be relatively high. The low level of production, however, makes the scheduling of reuse more difficult.

The large number of changes in dye type and shades means the value of HF concentrate collected from any one batch is small. The relative amount of residual dye left in mixing tanks and transfer lines is correspondingly large, however.

WASH WATER EFFLUENT COMPOSITION

Several classes of dyes are used at La France: direct, basic, disperse, acid and reactive, so the wash water effluent components vary in dye class and concentration. However, the types of components are common to all the wash water from the dyeing operations. The dye formulations contain dyes, a thickener (guar gum), surfactants, and in some cases, dye solvents. While about 85% of the dyes are exhausted on the fabric, the remaining dyes and most of the auxiliary components are removed from the fabric by the washing process.

In addition to the chemicals added to the fabric as dye formulation, there are significant quantities of material already on the fabric including natural waxes and oils and wetting agents and lubricant materials added in yarn preparation and weaving. All these chemicals are washed from the fabric and become part of the HF concentrate. The presence of these chemicals may influence the reuse. Table 3 presents a single set of results from extraction tests on (1) a sample of cotton fabric; greige and after dyeing and washing and (2) a sample of cotton and acrylic fabric; greige and after dyeing. Both types of fabric show that about 1 percent, on weight of fabric (owf) of water extractable material will be lost to the wash water. The cotton and acrylic fabric also indicates a loss of the wash water of more than 1 percent, owf, of waxes and oils.

Since the wash water flow rate is about 8 times the fabric rate, on a mass basis, the fabric contributes up to 0.3 percent, or 3000 mg/l, of total dissolved solids to the composite wash water. While the results of a single set of tests do not define the range of variation, they do indicate that the amount of material in the wash water can be significantly different from a simple dilution of the dye pad. The presence of the non-dye formulation materials in the HF concentrate may influence reuse.

Analysis of composite wash water effluent, the dye pad applicator residual, and the plant tap water, are presented in Table 5. Table 5 also shows representative concentrations for standard water flows from the washing section. The standard operation currently uses about 200 liters per minute and ranges up to 280 liters/min. The wash water effluent is characterized by being highly colored and quite "hard." The hardness is the result of chemicals added to the fabric because both the plant water and HF permeate are relatively soft. The wide pH range is indicative of the different dye types. The organic content of the wash water is indicated by the TOC and COD parameters. Most the dyes are exhausted onto the fabric and do not appear in

Table 3. Extraction Tests of La France

Sample No.	Description	Water Extractables, %owf(a)	Waxes and Oils (b), %owf(a)
1	Greige (cotton velour)	1.89	0.45
2	Green (As no .1 after dyeing (c)	0.91	0.46
3	Greige w/Brown and White Acrylic	1.80	3.48
4	Rust w/Brown and White Acrylic (As No. 3 after dyeing)	0.78	2.12

(a) owf = on weight of fabric
(b) Waxes and oils measured by trichloroethylene extraction AATCC Method 94.
(c) Dyed fabric have also been washed on the production dye range.

Table 4. Chemical Characteristics of the Dye Range Effluent

Assay	Average concentration or flow		
	Dye Pad	Composite[a] Effluent	Tap Water
Flow, ℓ/min.	12-35[b]	138	-
BOD, mg/ℓ	5,400	200	-
COD, mg/ℓ	23,900	1,200	9
Conductivity, µS/cm	1580-28,000[c]	200-2,000	90
Alkalinity, mg/ℓ	4,150	180	-
Color, ADMI	98,800	1,750	-
Hardness	-[c]	30	9
pH	3.6-10.9[c]	5.0-10.5	7.05
Phenols, mg/ℓ	0.84	-[d]	-
Total Solids, mg/ℓ	20,900	1,140	60
Suspended Solids, mg/ℓ	1,730	45	3
Dissolved Solids, mg/ℓ	19,200	1,100	57
Chromium, mg/ℓ	5.3	0.2	0.002
Copper, mg/ℓ	19.2	0.2	-
Iron, mg/ℓ	2.8	0.63	0.022
Manganese, mg/ℓ	0.2	0.1	-
Nickel, mg/ℓ	0.1	0.007	-
Zinc, mg/ℓ	2.7	0.25	-
Magnesium, mg/ℓ	10.4	8.5	1.00
Calcium, mg/ℓ	7.4	3.5	2.36
TOC mg/ℓ	6,250	325	-

(a) These are representative values based on measurements at various flow rates of wash water.
(b) Dye pad flow depends on cloth pickup. Pad drops are added directly to the HF concentrate without going through the HF unit.
(c) These values were estimated without averaging.
(d) Sample color interferes with analytical procedure.

the wash water. The fraction of the dye exhaustion onto the fabric is indicated, qualitatively, by a comparison of the color measured in the dye pad and in the wash water. Taking into account a dilution factor of about 8 to 1 by the amount of wash water at the time of the collection of these data, the exhaustion implied by the data in Table 4 is about 85 percent.

There is a significant quantity of dye pad solution remaining after each production lot. The quantity of dye mixed for each production allows for about 200 liters in a transfer line between the dye mixing room (drug room) and the pad. The composition of this excess dye liquor is the same as the dye pad with the exception of the suspended solids because a significant amount of lint from the fabric accumulates in the pad.

SECTION 5

REUSE

The principal objective of the operation of the HF unit during the initial period of the demonstration, through 1982, was to recycle hot water. The reuse of chemicals, dyes and auxiliaries, is important in providing a commercially attractive economic payout period. With sufficiently attractive rates of return on investments, the environmental quality benefits may be achieved as a by-product of closed cycle operation. The objective of the study during the extension period has been to develop a practical way to effect chemical reuse.

The study of chemical reuse has involved mixtures of HF concentrate and residual dyes of both direct dye (cotton fabric) and the basic (acrylic fabric) dye formulations. The study considered recovery from single production lots and mixtures accumulated from several lots of the same dye class. The reuse scenario recommended involves the use of the wash water from the dyeing of acrylics fabrics only. Currently these are the most valuable dyes in use at La France. If in the future other valuable dyes are used, the reuse scenario should be examined to include the most valuable recovery.

The reuse of the basic dyes from the production of acrylics may be expected to be less difficult than reuse of direct dyes because there should be less natural wax build-up from the cotton in the HF concentrate. The synthetic fibers are expected to contain no natural waxes and less synthetic size added in the weaving or preparation processes. The data from a fabric extraction test, Table 4, indicates the oils and waxes washed from the acrylic velours may be significant, however.

REUSE SCENARIO

The reuse scenario proposed is to process the wash water from acrylic fabric only. The configuration of the HF system during the full scale reuse evaluations is shown in Figure 4. Tanks permit 22,000 liters of wastewater storage and 3000 liters of concentrate storage. The membrane unit was able to process about 55 liters/min. of wash water.

The excess dye liquor in the pipe line from the drug room at the end of a production lot can be diverted directly to the concentrate storage tank.

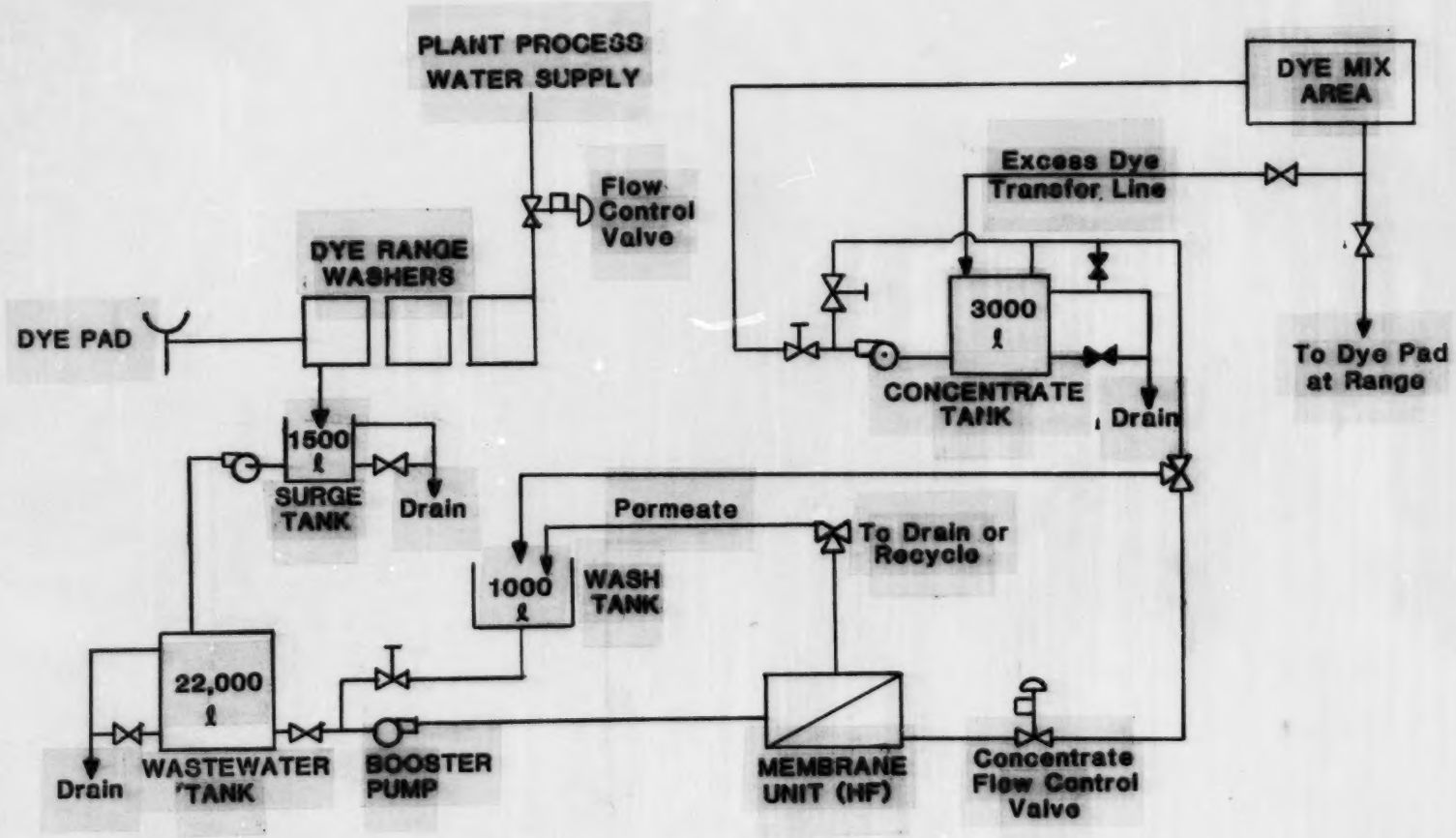


Figure 4. Recovery System Schematic. (All lines are stainless steel. All tanks are insulated fiberglass except the 1000 liter wash tank.)

If a total of 600 liters (3 lots) are allowed for pipe line volume, the concentrate tank can accommodate about 2400 liters of HF concentrate. This corresponds to 10 hours of operation of the HF system so that up to 33.000 liters of wash water can be processed. If washing is done with 280 liters/min., while the HF unit is operating at 55 liters/min., water can be collected for about 2.5 hours of production on the dye range in a single reuse batch. The 3000 liters of HF concentrate and dye liquor collected approximately equals the dye pad liquor volume needed for 3000 meters of fabric. At production rate of 20 meters/min. the production time to reuse the volume is also 2.5 hours.

A possible schedule for a typical daily routine of reuse is given in Table 5.

Table 5. Reuse Scenario Daily Routine

Second Shift

1. Range operator uses control panel switches to "collect" wash water and excess liquor for designated production lots.

2. HF unit automatically concentrates the wash water. Operation starts and stops based on liquid level in the 22,000 liter tank.

Third Shift

1. The second shift activity can be continued if indicated.

First Shift

1. HF unit operator mixes the HF concentrate tank and transfers a sample to dye mix room for initial strike.

2. HF unit operator flushes/washes the HF unit as required and leaves the unit set on "automatic".

3. Color matching for selected production lots is carried out.

4. HF concentrate and residual dye is transferred to designated mixing room tank (or tanks).

5. Dyes and auxiliary chemicals are added according to color matching formulation for scheduled production.

6. The production lots (probably not the lots in Step 5) are designated for "collection" on second (and third) shifts.

At the beginning of the first shift, the operator of the HF unit would find the concentrate tank full. This concentrate would be mixed and sampled for an initial strike (dyeing of a fabric sample) on the laboratory scale dye range. This initial strike would be the basis for color matching for full scale production to be scheduled on the second shift.

After taking this initial sample to the dye laboratory, the HF unit operator would proceed to flush the entire system and perform any membrane washing required. He would transfer the HF concentrate and dye residue mixture to the appropriate dye mixing tank (or tanks) upon instructions based on the color matching results. Overall it is estimated that the operator would be able to completer these tasks in about 4 hours of the first shift.

The color matching for reuse would ideally be directed to production scheduled for the second shift. Reuse would involve the production of about 3000 meters of fabric in one or more lots. The HF concentrate and excess dye residue would be used in preparing the dye formulations for the selected production lots. Production procedures are not altered in any way. The dye mix is prepared to shade based on the initial test strike and manual, or computer, determined dye additions to achieve a color match to a scheduled production shade.

At the end of the first shift, the dye mixes for reuse will be complete for second or third shift production. Also the HF unit will have been cleaned and set on automatic, ready to receive and begin processing the next batch for chemical recovery.

The production schedule will also designate the production lots on the second shift that will be collected for reuse.

TEST RESULTS

Seven tests were conducted to demonstrate the technical feasibility of using the HF concentrate to formulate standard production shades. The HF concentrate was mixed, prior to reuse, with approximately equal amounts of excess dye formulation solution. Both the HF concentrate and excess formulation were collected from production lots. All materials used in these seven tests were processed through the full-scale recovery system. The description of these tests and results are tabulated in Table 6.

Two types of tests were carried out. Four tests involved the collection of the wash water and excess dye from a single production lot. Three tests involved the collection of wash water and excess dye from several production lots so that the reuse material was a mixture. In two of the tests in which the wash water ws from a single lot, the resue test was to dye the same color from which the wsh water was collected and in two cases the reuse was to colors of similar shade. Three of these tests involved direct dyes and one involved basic dyes. (Basic dyes are actually a proprietary mixture of two types of dyes and auxiliaries for acrylic fiber fabrics.) The three tests with mixtures included two tests with direct dyes; one with basic dyes.

Table 6. Test Dyeing with HF Concentrate Mixed with Approximately Equal Portions of Excess Dye Liquor

Date	Test Mixture	Standard Shade Produced	Results
8/8 8/15	single lot, direct dye, c/686	c/617(a); blue; 450 m	lab scale color matching, crock test acceptable; 50% aux. chemicals; 7 production adds
8/15	mixture of basic (b) lots c/2362, 6642,7752,6772, 715,6692	c/685; slate; 550 m	lab scale color matching; crock test acceptable; 50% aux. chemicals; 2 production adds
8/19	mixture of direct dye lots c/3255,325	c/334; brown; 4500 m	lab scale color matching; crock test acceptable; 50% aux. chemicals; computer calculated dye adds; HF conc. diluted 2 to 1 before dye addition
8/25	single lot of direct dye, c/686	c/686; slate; 4500 m	lab scale color matching; crock test acceptable; 50% aux. chemicals; computer calculated dye adds; HF conc. diluted 2 to 1 before dye addition; 2 production adds
9/2	single lot of direct dye, c/686	c/686; slate; none	computer calculated dye adds; HF conc. diluted 2 to 1
9/21	mixture of direct dye lots c/3255,434,4375	c/434; rose; none	computer calculated dye adds
10/18	single lot of basic dye c/2462	c/2362; rust; 450 m	lab scale color matching; crock test acceptable, 50% aux. chemicals; off-shade production required redye

(a) c/xxx indicates production color that is achieved by proprietary mixtures of dyes and other chemicals.

(b) basic dye refers to proprietary mixtures of basic and other dyes and appropriate chemicals for acrylic fiber fabric.

The results of these tests demonstrate the technical feasibility of reuse of both mixtures and single lot recovery. The production at La France is characterized by frequent changes in dye lots. The many production lots involve a wide variety of colors and two types of fabric. The small-lot production makes it important to verify the feasibility of the reuse of mixtures of wash water and excess dye from several lots. Since the basic dyes do not stain cellulosic fibers and direct dyes do not stain acrylic fibers, it is possible to mix dye types as well as colors when appropriate auxiliary chemicals are present. Laboratory scale tests confirmed this reuse of mixtures during an earlier phase of this project (5). No full-scale reuse of mixtures of direct and basic dye product lots was attempted, however.

Initially all the color matching was done manually in the production laboratory. The color matching computer was being installed during the final weeks of this project extension period. Because of the large amount of empirical data required by the computer program, correspondence between computer calculation and production results was still being refined. Because of the projected market, the computer was not scheduled to be programed for basic dyes before 1984.

In all reuse tests only 50% of the normal amount of auxiliary chemicals was added in the reuse formulations. Most of these auxiliary chemicals are washed from the fabric and are concentrated by the HF for recycle. Previous (5) laboratory scale data indicated that probably only 25% of auxiliary chemicals would need to be added. These current full-scale tests were conservative in this aspect.

Another interesting aspect of reuse was illustrated in the tests on 8/19, 8/25, and 9/2. In these three cases the HF concentrtate was diluted prior to reuse. In the test on 8/19 the dilution was required because at least one of the primary colors was present in the HF concentrate to a level higher than needed in the standard shades to be dyed in reuse. In the tests on 8/25 and 9/2 the reuse was to the same shade but the dilution was required to achieve the volume of liquid needed for the production lot size.

The number of production adds, the color adjustments made after production starts in the reuse tests, was the same as normal except for the one case of seven adds. Technical feasibility of reuse was demonstrated by these test results. The economic practicality depends on the value of dyes, production lot size and the capacity of the HF unit. The economic aspects are discussed below.

POTENTIAL SAVINGS

Based on 1981 prices the cost of chemicals and dyes used at La France with acrylic fibers is presented in Table 7.

Table 7. 1981 Cost of Basic Dye Formulations

Shade	(¢/l) Dyes	(¢/l) Chemicals
Heavy	53	32
Light	28	14

The production of acrylic fabric varies from week ot week. The production of three weeks in 1983 is tabulated in Table 8.

Table 8. Fabric Production

Week Ending	Yards	Yards/Day
July 4	7,392	1837
June 30	25,256	3607
June 6	12,712	1897

To calculate the potential savings it is assumed that the dye exhaustion is 80% even on heavy shades. The 'exhaustion' or loss of auxiliary chemicals has been estimated in previous laboratory tests (5) to be about 25%. Production data indicate the average production lot of acrylic fabric to be about 750m. At an average production rate three lots of heavy shade would yield for reuse the savings listed in Table 9.

Table 9. Potential Savings for Three Average Production Lots of Acrylic Fabric

Wash water collected	24,000 liters	
Dye pad solution used	2,475 liters	
Excess dye solution (3 lots)	600 liters	
	Heavy Shades	Light Shades
Dye in HF concentrate	$236	$125
Chemical in HF concentrate	534	233
Excess dye & chemicals collected	510	252
Potential Savings	$1280	$610

If the average between light and dark shades is assumed, the potential savings for 300 days is $283,500/year. Because of difficulty in scheduling to reuse all the dyes collected, an estimate of practical reuse is taken as 50 percent or $141,000/year.

Clearly the HF system can be operated very profitably as a chemical recovery. The current equipment, with two additional concentrate storage tanks (estimated at $2,500 each) could repeat this reuse scenario each shift instead of just once per day.

The significant costs to operate the recovery system are the electricity for pumps, labor and service fee. The costs are tabulated in Table 10.

Table 10. Operating Costs (a) Estimates

Utilities	$/hr.	$/yr.
Steam (@ $6/$10^6$ BTU)	2	2000 (b)
Electricity (3.5 /kw/hr)	1	2400
Labor (c)	8	4000
Membrane Service (d)		14000
	Total	28400

(a) Reuse scenerio requires 6 hours of operation plus 2 hours cleaning each day.
(b) Heat exchangers can be used to reclaim this energy.
(c) Labor is 4 hours each first shift.
(d) Service contract fee.

SUMMARY

The HF recovery system if used only for chemical recovery with selected production lots can produce significant savings. At 1981 production levels of acrylics fabric (heavy and light dye shades) the annual savings could reasonably be expected to be equal to or greater than $141,000/yr for one-shift operation.

To achieve these savings, operating costs of about $28,400/yr would be incurred. These operating costs are about 20% of the savings.

If production of acrylic, nylon, or other fabrics that use expensive dyes and auxiliary chemicals in the pad formulations should increase, the current HF equipment can process three times the chemcials as assumed in these estimates.

SECTION 6

RECOVERY SYSTEM CONFIGURATION

The recovery system was designed to collect all water from the dye range and to transfer this fluid to the hyperfiltration (HF) unit. The permeate from the HF unit is collected for recycle to the range as hot wash water and the concentrate is collected for reuse or disposal.

A design report has been issued separately (6). The configuration used throughout was described in detail in the project report (1). In the discussion which follows, the design as modified for chemical recovery without water recycle, is presented.

DESIGN

The equipment arrangement is schematically presented in Figure 4. The wash water is pumped at high pressure through the membrane unit. The concentrate flow can be controlled in the range of 4 to 20 liters per minute. The concentrate flow rate is selected to achieve the volume reduction needed to permit a match with the volume of dye formulation to be employed in reuse.

The permeate flow is directed to drain since in this factory the most valuable chemicals are basic dyes for which the ZOPA membranes yield permeate unacceptable for general reuse (1).

The wastewater tank has a volume of 22,000 liters. This volume permits collection of the wash water from about 3 hours of production on the dye range when the hyperfiltration unit operating at the same time. This time period is long enough to capture all the effluent from the largest production lots or three of the average lots.

The hyperfiltration of this wash water can be set to produce as little as 1000 liters of concentrate. The hyperfiltration concentrate is collected in the 3000 liter storage tank. At the end of each production lot, the excess dye in the transfer line and drug room mixing tank is transferred directly to this 3000 liter storage tank. The hyperfiltration concentrate and the residual dye, that may be in approximately equal volumes, is stored in the concentrate storage tank.

The washer section of the dye range employs counter-flow washing with the overflow to drain from the jet washer. The flow scheme is as shown in Figure 4. The drains and overflows are collected in a sump and pumped to the wastewater tank. (A vibrating screen is being installed just upstream of the surge tank because during system draining the wastewater bypasses the rotating screen filters associated with each recirculating washer unit). This detail of the drain system is omitted from Figure 4 for clarity.

The flow rate to the dye applicator from the drug room depends on the range speed. The design assumes 1 liter of dye solution is added for each meter of fabric. The amount of dye solution mixed in the drug room depends on lot size because the 140 meters of leader on each end of each lot does not require dye solution.

OPERATIONAL MODE

Conceptually, the cycle of operation for chemical recovery begins with wash water from the 140 meter fabric leader overflowing the surge tank to drain. As the velour fabric enters the washers, the operator starts the surge pump and the wash water is pumped to the 22,000 liter collection tank. The surge pump is stopped about 5 minutes after the trailing edge of the fabric exits the washers.

The HF unit starts automatically when the liquid level in the 22,000 liters wastewater collection tank reaches a set-point. Operation of the HF unit continues until the liquid level in the wastewater collection tank falls below a set-point. The HF unit operator will manually flush the recovery system prior to collection of the wash water from production lots selected for recovery. When the fabric trailing edge passes the washers, the operator may elect to drain the wash boxes or allow wash water to continue to flow, or stop the wash water depending on the next color to be dyed.

HF UNIT CONFIGURATION

The HF unit is a Single Pass system (Patented)* consisting of zirconium oxide-poly(acrylic acid)(ZOPA) membranes dynamically formed on the interior of 70 bundles of sintered stainless steel support tubes. The 70 bundles are contained in ten modules. The total membrane area is 139 m^2 (1,500 ft^2).

The high pressure flow from the positive displacement pump enters a manifold which distributes the flow into an initial section comprised of four parallel flow paths of 1.6 cm diameter tubing. The four streams from this section are collected in a manifold and divided into three parallel flow paths in the second section of 1.6 cm tubes. Similarly the third section has two parallel paths and the the last section has one. The last two sections contain 1.3 cm diameter tubes. Each flow path has several segments of tubing

* U.S. Patent No. 4200533

connected in series. The flow path lengths are indicated in Figure 5(a) where the tapered arrangement of the flow path is depicted.

The flow arrangement was designed to yield low velocity, low pressure-loss system through the 1.6 cm diameter tubing. When concentration becomes high enough to produce a significant velocity effect, 1.3 cm diameter tubing has been used to increase the fluid velocity. The velocity range in the 1.6 cm diameter tubing was designed to be 1.5 - 2 m/sec and in the 1.3 cm tubing was 2 - 3 m/sec. A photograph of the HF unit is shown in Figure 5(b).

The key components of the recovery system are shown in Figure 4. The recovery system piping is 304 stainless steel. All tanks are fiberglass except for the 1000 liter stainless steel wash tank for the HF unit. These materials are corrosion resistant over a wide range of pH and temperature consistent with the dye range equipment. The transfer pumps are stainless steel single-stage centrifugal pumps. The pipe and pumps sizes are chosen to permit transfer not more restrictive of process time than were already the production standard.

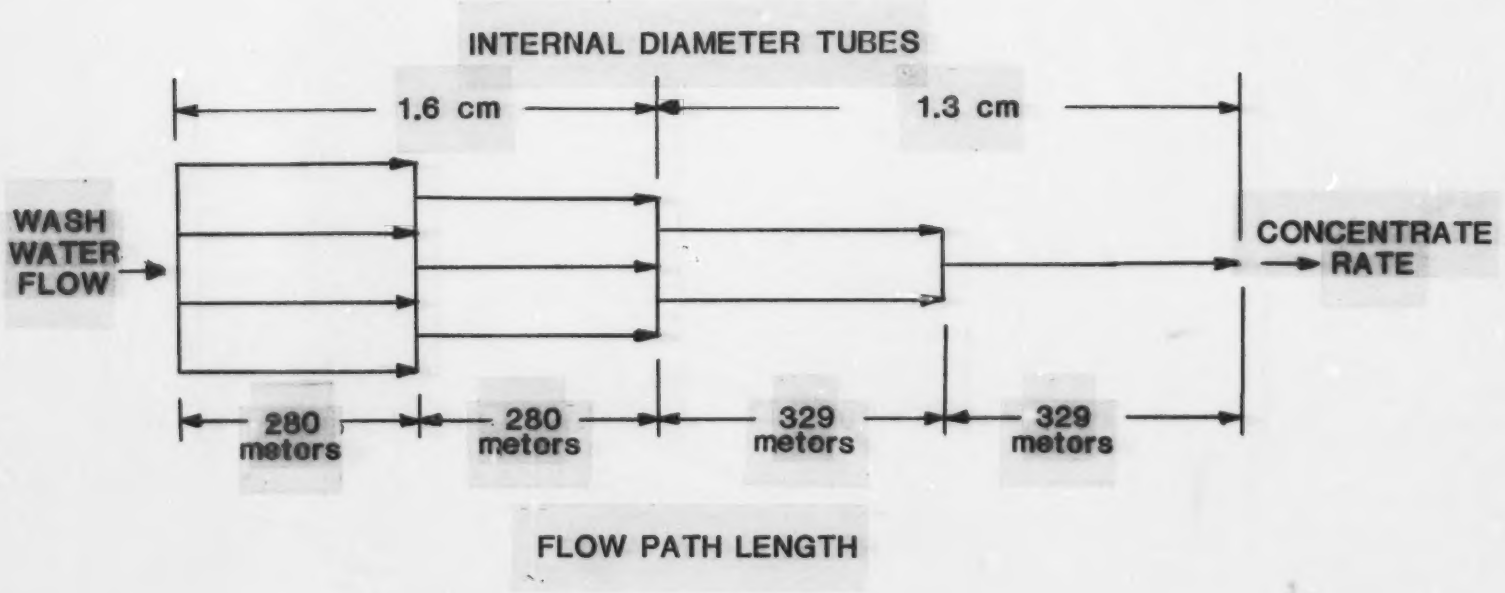


Figure 5(a). Single Pass Membrane Unit Flow Configuration. (Each arrow represents a flow channel. The tapered configuration is 4 to 3 to 2 to 1 parallel flow channels connected in series.)

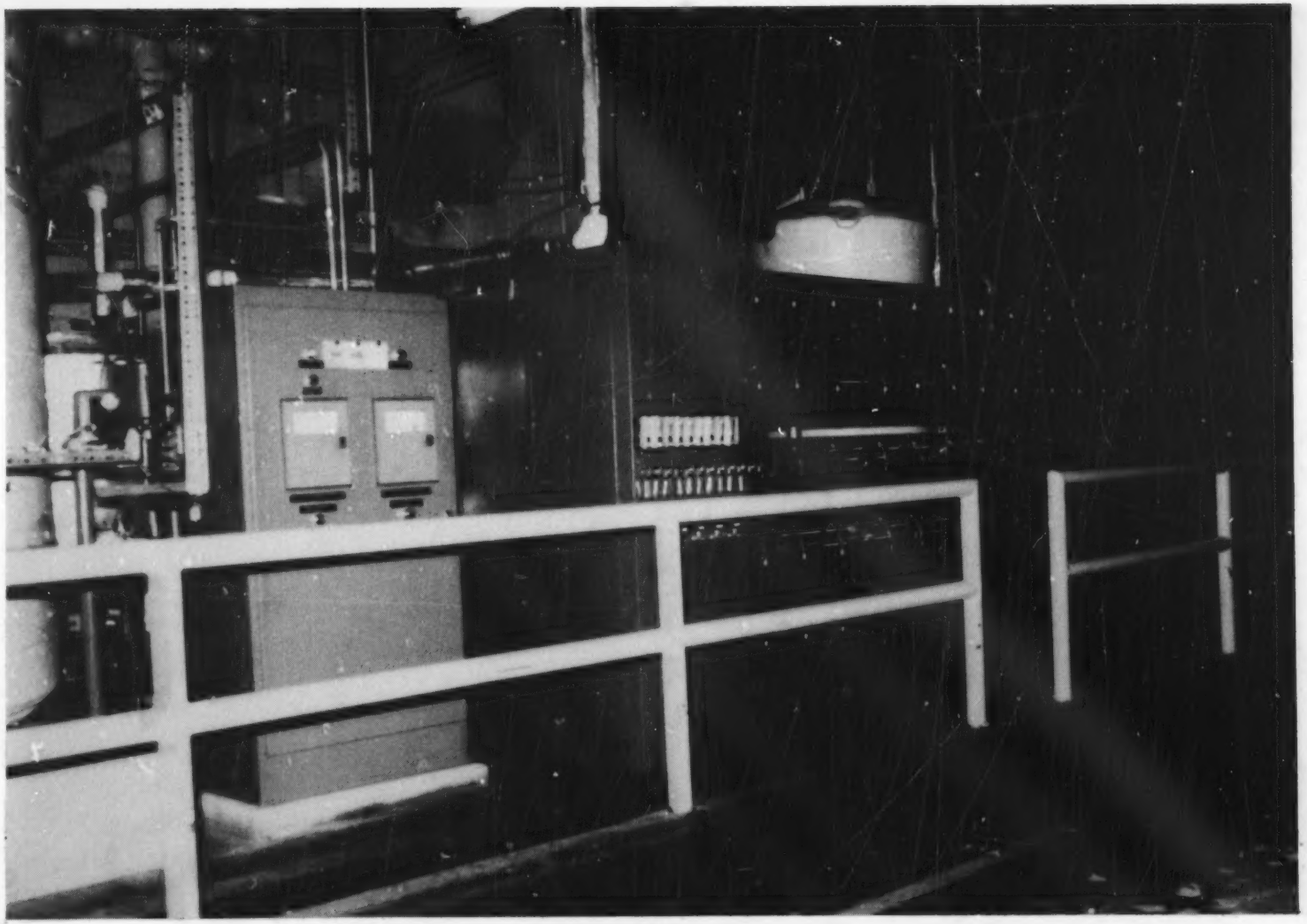


Figure 5 (b). Hyperfiltration Unit at La France.

SECTION 7

HF UNIT PERFORMANCE

The performance of the HF unit for chemical recovery is judged in terms of the quantity of wash water that can be filtered and the yield in terms of percentage of desired chemicals contained in the HF concentrate.

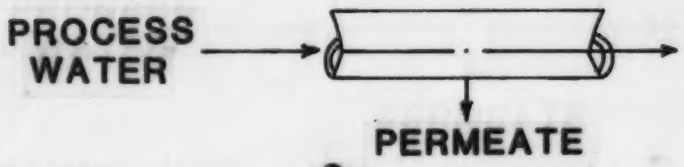
The study of membrane cleaning continued during the 12 month extension period. Cleaning procedures specific for direct dye and for basic dye formulations were developed. A module containing 15 m^2 of membrane was stripped and recoated on-site to demonstrate this capability of the dynamically formed membranes.

CHEMICAL RECOVERY YIELD

The retention fraction achieved by a membrane is defined as rejection. This definition is illustrated in Figure 6(a) for a differential membrane element. The Single Pass membrane system is illustrated in Figure 6(b). The yield of chemicals recovered is obtained by multiplying the concentration of the species in the HF concentrate by the fraction of the initial volume recovered as HF concentrate. The equation for yield is given in Figure 7(b).

For the basic dyes and the direct dyes the rejection is 0.96 and 0.99 respectively. The reuse scenario has a recovery of 2400 liters from a wash water volume of 33,000 liters; i.e., R = 0.93. The yield for direct dyes is thus 0.97 percent, i.e. 97 percent of the dye in the wash water is retained in the HF concentrate. Only 3 percent passes through the membrane with the permeate. For basic dyes the yield is .90, i.e. 90 percent of the dye in the wash water is retained in the HF concentrate. However, 10 percent passes through the membrane with the permeate. The 90 percent yield is sufficient for effective chemical recovery while the 10 percent loss makes the reuse of permeate difficult.

For both direct and basic dye formulations, initial laboratory tests (6) indicate that 50 to 75 percent of the auxiliary chemicals can be saved when formulating dye solutions with HF concentrate. The yield of each of the species is different, e.g. guar gum is retained nearly 100 percent while surfactants may be retained at closer to 50 percent. Because of the low value of these auxiliary chemicals as well as the insensitivity of the production quality to wide variations in their amount, a careful evaluation of rejection, hence yield, has not been made.



$$\text{REJECTION, } \gamma = 1 - \frac{C_p}{C}$$

C = Process Water Specie Concentration

C_p = Permeate Specie Concentration

Figure 5(a) Differential Membrane Element.

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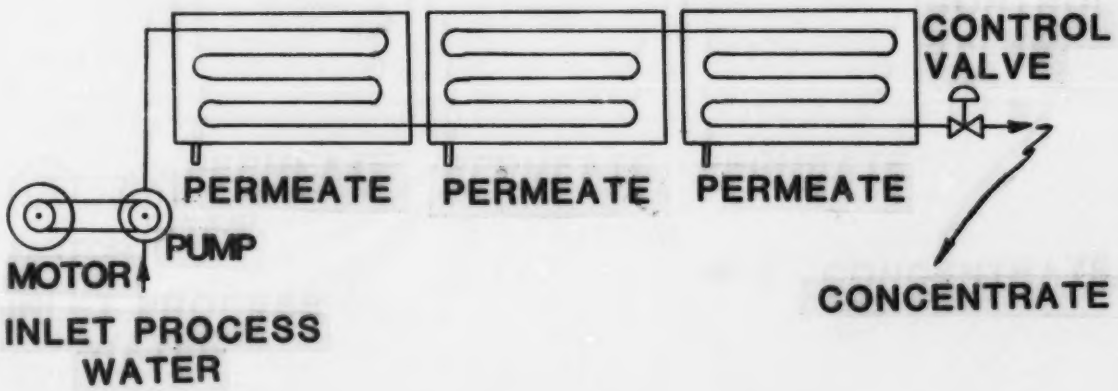

$$\text{RECOVERY, } R = \frac{\text{Volume Flow of Permeate}}{\text{Volume Flow of Inlet Process Water}}$$

$$\frac{\text{Composite Permeate Specie Concentration}}{\text{Inlet Process Water Specie Concentration}}, \frac{C_p}{C_f} = \frac{1 - (1-R)^{\gamma}}{R}$$

$$\frac{\text{Concentrate Specie Concentration}}{\text{Inlet Process Water Specie Concentration}}, \frac{C_c}{C_f} = (1-R)^{-\gamma}$$

Figure 5(b). General Single Pass Membrane System Arrangement.

MEMBRANE FLUX

The quantity of permeate generated by the recovery system is a function of the operating conditions at any given moment and a function of longer term effects such as fouling and possible membrane modification including deterioration and chemical reactions.

The quantity of permeate generated is expressed as membrane flux (i.e. the volume of permeate per unit of membrane area per unit of time). Common units are $m^3/m^2/day$ or m/d.

Effects of Operating Conditions

The principle operating conditions that are known from the design phase of this project (5) to have essentially an instantaneous effect on membrane flux are temperature, pressure, and concentration of gum. The flux increases rapidly with increases in temperature. Approximately the flux doubles with an increase in temperature of $25^{\circ}C$. The flux increases linearly with pressure up to a limiting value that depends on the presence of macromolecules, e.g., gum. Depending on the concentration of gum, there may also be an effect of fluid velocity. A mathematical model describing the effects of the gum on membrane flux has been developed (6).

Effects of Membrane Fouling

Membrane fouling is defined as a decrease in flux that is not an instantaneous reversible effect of pressure, temperature, velocity, concentration, or other controlled operating variables. Fouling is usually categorized as (a) an alteration in the membrane due to chemical reaction with the waste stream or (b) an accumulation of a deposited layer. An example of alteration in the membrane is reactions between the charged membrane and metal ions Cu++, Mg++, Ca++, Fe++, etc. that commonly occur in the wash water. Reactions can also occur with polymers. For example, the ZOPA membranes are particularly sensitive to cationic polymers. Examples of the type of deposits that may occur at La France are:

(1) undissolved dye particles
(2) calcium carbonate, or similar insoluble compounds of the metals
(3) undissolved fraction of the guar gum which could form a carbohydrate film
(4) fine lint and other suspended solids, perhaps in combination with the gum
(5) the insoluble reaction products of basic and direct dyes (the two major classes of dyes in use on the dye range)
(6) silicone and other oils used as anti-foam agents, and
(7) biological material that may form in the storage tanks.

Because the removal of foulants depends on the nature of the foulant, membrane washing procedures must be selected to attack one or more of the types of fouling. The sequence of cleaning is also important, for example an acid pH may precipitate a chemical easily dissolved in base.

MEMBRANE CLEANING

The cleaning procedure must be directed to remove the foulants. The principal foulants expected are waxes and oils from the natural fibers or the manufacture of the fabric, the gum used as dye solution thickener, dye particles, and metal oxides or hydroxides. Two distinct procedures were developed: the first for the basic/direct dye mixtures and the second for the pure direct dye formulations. The second is also applicable to fouling resulting from processing reactive dye.

The cleaning solution contains surfactants for the removal of deposited suspended materials. A solvent is included to remove waxes and oils. The pH is adjusted so the solution will serve as a solvent; low pH (pH = 4.5) as a solvent for basic dyes, gum and also for many of the inorganic precipitants, high pH (pH = 9) as a solvent for direct dyes.

Cleaning Procedures

The cleaning procedure for direct dyes is presented in Table 11. The same solution would be used for reactive dyes. The cleaning procedure for the blends of basic and direct dyes is presented in Table 12. The cleaning chemicals are similar for both procedures but the order of their application is different.

To clean the system after processing basic dye/direct dye mixtures, the system is initially flushed with hot water at low pH (pH = 5). The solvent and surfactant solution is also used at low pH. Finally the system is washed at high pH (pH = 9). The final flush is with hot water at 90°C.

To clean the system after processing direct dyes or reactive dyes, the initial flush is just with hot water. The solvent and surfactants are used at high pH (pH = 9). The final wash is at low pH (pH = 4.5) adjusted with citric acid and NH^4OH. The final step is to flush the system with hot water (90°C).

Test Results

To avoid the accumulation of a complex mixture of all types of foulants, the reuse scenario includes daily cleaning. This recommendation is based on test results obtained with daily washing and without daily washing. These test results are summarized in Table 13. The test began with a completely cleaned system. After cleaning the system was operated for 3.3 hours with wastewater accumulated from three direct dye production lots. The system was flushed with hot water (90°C) the next day and operated for 5.25 hours on more wash water from direct dyes. The following day the unit was flushed

Table 11. Membrane Cleaning Procedure for Direct or Reactive Dye Formulations

1. Flush system with 1000 liters of hot water (90^{o})

2. Fill 1000 liter wash tank with water and add in order:

   3 liters of Butyl
   80 ml of Triton X-100
   80 ml of Servitol WXCS
   120 g Sodium Carbonate (to pH = 9.5 $\pm$ 0.5)

3. Heat to 90^{o}C with steam injection

4. Pump solution through system to drain with concentrate controlled at 20 liters/minute

5. Repeat (2) - (4)

6. Fill 800 liter wash tank with water and add 150 ml of acetic acid (pH = 4.5 $\pm$ 0.5)

7. Heat to 90^{o}C with steam injection

8. Pump solution through system to drain with concentrate flow controlled at 20 liters/minute

9. Repeat (6) - (8)

10. Flush system with 1000 liters of hot water (90^{o}C)

Table 12. Membrane Cleaning Procedure for Basic/Direct Mixture Dye Formulation

1. Fill 1000 liter wash tank with water and add 35 ml of acetic acid then heat to 90°C
2. Pump solution through system to drain with concentrate flow set to 20 liters/minute
3. Repeat (1) and (2)
4. Fill 1000 liter wash tank with water and add, in order:

   3 liters of Butyl
   80 ml of Triton X-100
   80 ml of Servitol WXCS
   100 ml of acetic acid (pH = 5.0 + 0.5)

5. Heat to 90°C with steam injection
6. Pump solution through system to drain with concentrate flow controlled at 20 liters/minute
7. Repeat (4) - (6)
8. Repeat (1) - (2)
9. Fill 1000 liter wash tank with water and add 125 g of sodium carbonate (pH = 9.5 ± 0.5) then heat to 90°C
10. Pump solution through system (see (6)
11. Repeat (9) - (10) and then flush with hot (90°C) water.

Table 13. Membrane Cleaning Frequency 'Test Results'(a)

Day	Membrane Wash	Wastewater Dye Type	Conc.(g/l) (b)	Duration (hrs)	System Capacity (c) Average	At 1 hour
0	-	Mixed		-		
1.	Table 6	Direct	25/1.2/1.8	3.3	3600	4080
2.	Hot Water	Direct	1.2	5.2	2880	3600
3.	Hot Water	Direct	14/1.5	3	2400	2640
4.	(d)					
5.	(d)					
6.	(d)					
7.	Table 6	Direct	24/0.4	4	2640	4320
8.	Table 6	Basic		1	3600	3600
9.	(d)					
10.	Table 7	Basic	1.6	2.7	4080	5280
11.	Table 7	Direct	0.5/5/0.3	2.7	3600	5280

(a) The membrane washing occurred each day prior to the processing wastewater and thus was selected for the previous days wastewater type.
(b) Concentration is listed in g/l for each of the dye lots from which wash water was collected.
(c) System Capacity (l/hr): The average capacity for the duration and the capacity after 1 hour of processing with waste.
(d) No operation: HF unit was shut down with wastewater in the tubes.

again with hot water (90°C) and operated for 3 hours on additional direct dye wastewater. The following week a similar sequence was carried out except that the complete washing procedure appropriate to either direct dyes or basic/direct dye mixtures was carried out each day.

Because the operating periods on the wastewater varied widely from day to day, the flux one hour after initial exposure is tabulated as the parameter for comparison. The membrane flux drops very rapidly after initial exposure to the waste and remains fairly constant for several hours.

The membrane flux in nominal units is presented in Figure 7 versus time after exposure to waste wash water for several of the tests used to evaluate washing frequency. The data are taken from the recordings of rise in the liquid level in the 22000 liter permeate storage tank. There is some inaccuracy in the zero point of time. The nominal unit of membrane flux is simply the change in liquid level in a one-half hour interval.

The data for days 1, 7 and 11 indicate the nature of the flux decline with time when the membranes have been cleaned just prior to exposure to waste. Comparison of the data from day 2 with data from days 1, 5 and 11 suggest that a hot water flush may restore membrane flux. However, the data from day 3, two days after a complete wash, indicate that a hot water flush is not adequate in the absence of frequent complete washings.

The results in Table 13 indicate a significant decrease in the membrane flux from day to day when complete cleaning was omitted. The flux is maintained at a reproducible level completely by washing on a daily basis. The data were examined to determine the influence of these other parameters: the duration of the period of operation with waste, the concentration of dye in the wastewater and the type of dye(s) in the wastewater. The most pronounced and systematic effect is the number of days since the last cleaning.

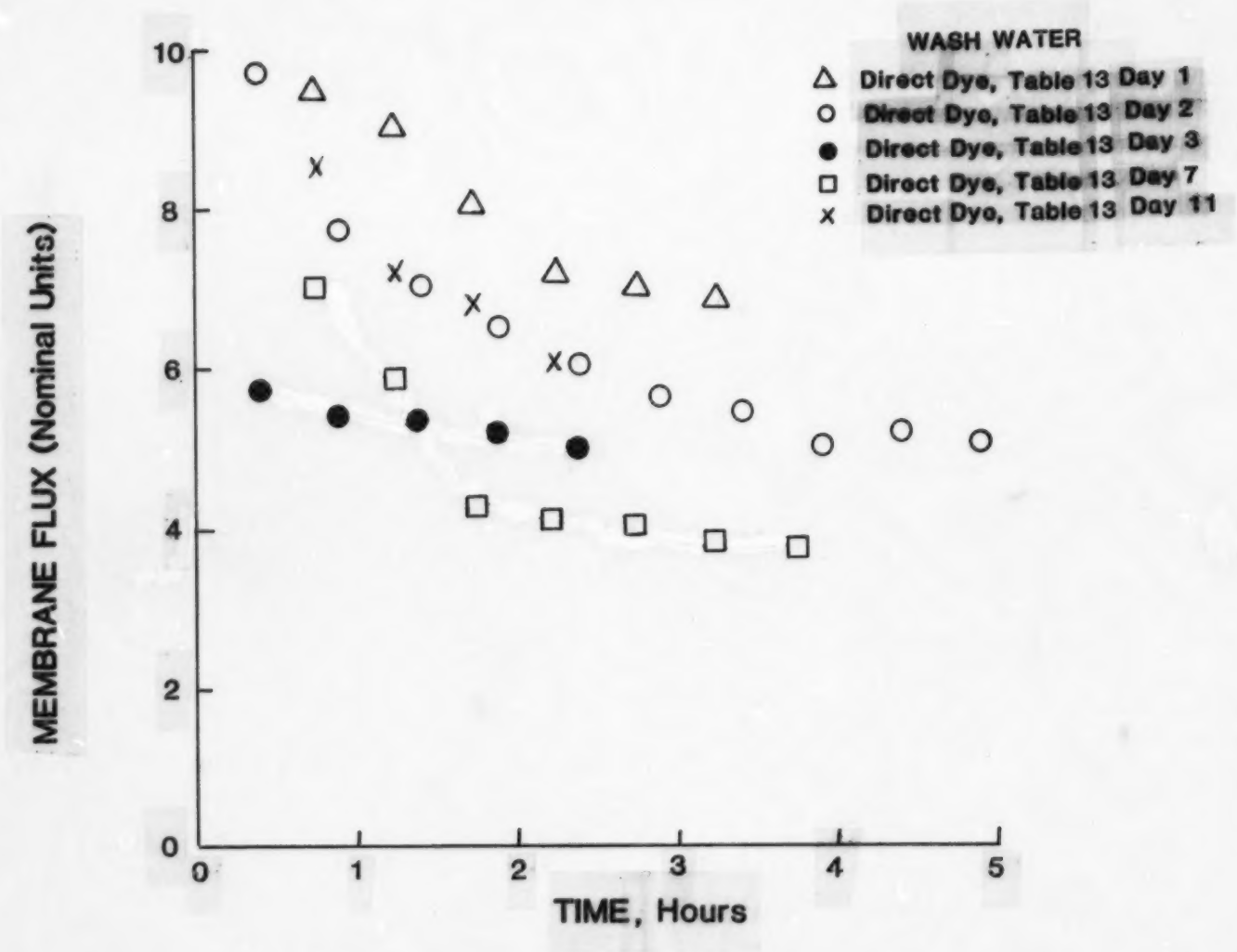

Figure 7. Membrane Flux versus Time After Exposure to Waste Wash Water.

MEMBRANE STABILITY

Membrane stability is judged by the color rejection because color in the permeate is easily observed and can be accurately measured. In fact, the sensitivity of color rejection is such that a change from 99 percent rejection to 98 percent is easily discernible. During the first 13 months there was no indication of membrane deterioration (6). Intermitten service during the subsequent more than 18 months there have been no indications of membrane deterioration. The color rejection of the reference blue direct dye has remained greater than 97 percent for the system average.

HF UNIT AVAILABILITY

During the period of this extension the on-stream demand for the HF unit has been low since it has been used primarily as a test unit in the study of dye and chemical reuse. One aspect of availability for dynamically formed membranes is the potential for in-situ formation. Dynamic formation of membranes implies that the membranes may be replaced, with the same or different membranes, on-site utilizing the HF unit in the washing mode.

During the first 13 months of this demonstration project, the procedure of stripping the membrane and recoating the stainless steel tubes was carried out several times (6). During this extension period, on-site membrane replacement was demonstrated.

Module no. 6, containing 280 meters of 1.6 cm diameter tubes was selected to demonstrate the in-situ on-site reformation. Module No. 6 was originally placed in service on March 3, 1981, and had been in continuous service since one of seven bundles was replaced on September 24, 1981 (6).

The procedure of recoating module no. 6 involved rearranging the piping so that only this module was connected to the pump. Both the permeate and concentrate were routed back to the 1000 liter wash tank. The initial steps in the procedure were a complete cleaning including both the washing procedures in Tables 12 and 13. After complete cleaning, the old membrane was chemically stripped and the recoated following proprietary procedures.

Module no. 6 was stripped and recoated three times in May, August, and October 1983. Each time the ZOPA membrane was replaced in-situ. Each time additional proprietary membrane coatings were applied in an effort to increase rejection of basic dyes or to decrease the fouling rate. Basic dye rejection was increasaed by each of the proprietary coatings from 90 percent to about 98 percent. The flux level was not improved by either new membrane.

While the research into tailoring membranes in-situ did not fully meet the objectives of 99 percent rejection of basic dyes and decreased flux decline rates, the success of in-situ formations has encouraged a continua-

tion of these research efforts with private fundings. The demonstration of these abilities to reform membranes is an important success for this project because it verifies the implied long-operating life claimed for the sintered metal membrane system. Original projection (5) called for semi-annual remembraning by returning the modules to the factory. No membrane replacement has been required in the 3 years since the first modules were placed in service. The demonstration of on-site membrane formation and the obvious convenience will lead to consideration of recoating for improved performance, not just when required because of some eventual deterioration.

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